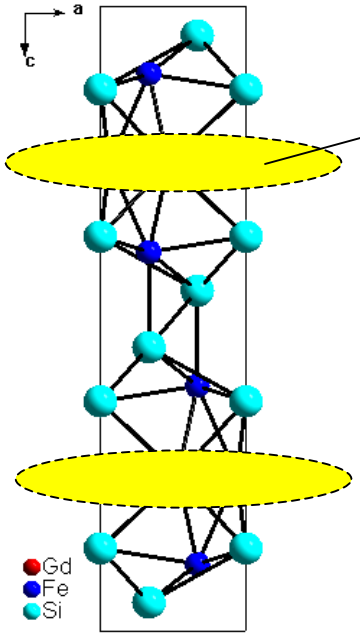
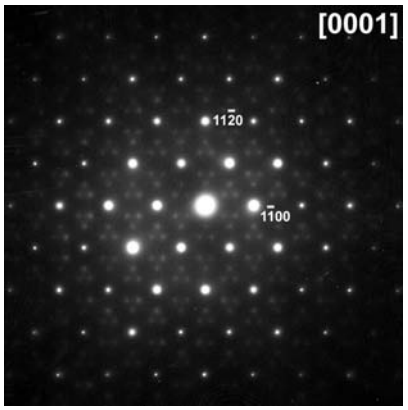
# Linking Intermetallics and Zintl Phases (DMR-0241092)

Gordon J. Miller, Iowa State University

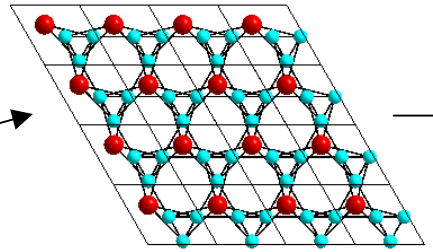
**GOAL:** establish structure-bonding-property relationships for complex intermetallic compounds in order to tailor new compounds with desired features.

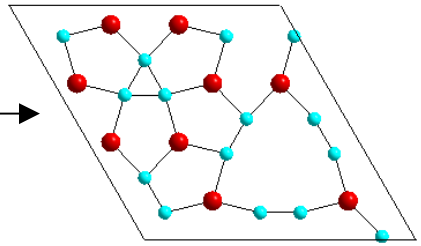
**HIGHLIGHTS** from 1-Oct-2003 – 30-Sep-2004



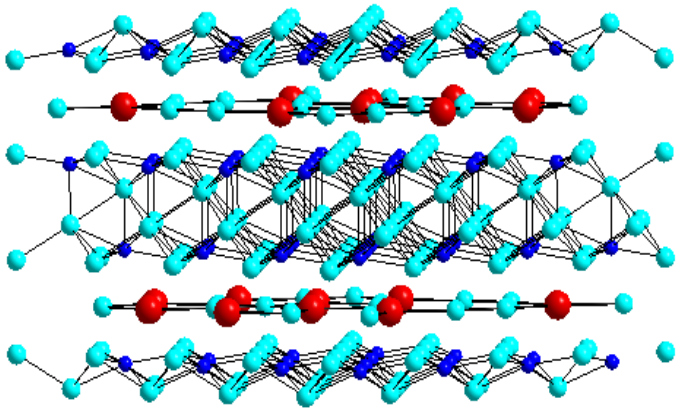

**Electron Diffraction**





4×4 Superstructure

$FeSi_2$



$Gd_{1.2}Fe_4Si_{9.9}$

**Superstructures in a New Intergrowth Structure:** We use XRD, electron diffraction and *ab initio* calculations to understand new intergrowth structures involving $FeSi_2$ and rare-earth silicide nets. We have discovered a 4×4 superstructure which accounts for the "nonstoichiometry" and other properties in $RE_{1.2}Fe_4Si_{9.9}$ (RE = Gd, Er, Yb, and Y).

The Miller Group at Iowa State University studies complex intermetallic compounds using experiment and theory, which include synthesis, structural characterization and physical property measurements (resistivity and magnetization) coupled with *ab initio* electronic band structure calculations. Theory helps us identify new targets with possibly interesting properties. In this slide, I highlight three important aspects of our work this past year.

(Left) Flux synthesis of rare-earth/Ta/Al compounds in Al fluxes led to the growth of large single crystals of $TaAl_3$. Calculations on $TaAl_3$ shows a pseudogap in the density of states at the Fermi level and gave us motivation to prepare the pseudobinary, $TaAlGa_2$, which shows semiconducting behavior (small band gap) and may have interesting magnetoresistive behavior. Semiconductivity in close-packed metals is very unusual, but, in this case, is related to the nature of the main group element clusters formed in this structure. (Red = Ta; Al and Ga form pyramids.) These results may provide interesting new materials for metal-semiconductor junctions. One paper is currently in press in Inorganic Chemistry; the work was performed by graduate student, Cathie Condron.

(Center) We are studying materials with applications to magnetic refrigeration – these include $LnFe_{13-x}Si_x$ and $LnFe_{13-x}Al_x$, which form 3D networks of mixed-metal icosahedra. As the variable x increases, there is a tendency toward increasing order so that repulsive Si-Si or Al-Al interactions are minimized. At sufficiently high x, the structure changes from cubic to tetragonal. Magnetic measurements suggest that only the cubic phases are candidates for magnetic refrigeration. This work is part of the Ph.D. thesis of Mi-Kyung Han.

(Right) Examination of structures containing icosahedra led us to an examination of Mn-containing intermetallics. GaCr, GaMn and GaFe form a series of isostructural compounds based on chains of icosahedra. Again, calculations revealed a change in magnetic behavior and experiment confirmed that GaCr is antiferromagnetic at low temperatures, GaFe is ferromagnetic and GaMn shows a complex magnetic behavior. Thus, we have a series of isostructural compounds with different band fillings to study the relationship between valence electron concentration and magnetic behavior. One paper was published in the Journal of Solid State Chemistry; one is being reviewed by the Journal of the American Chemical Society. This work was performed by post-doctoral associate Olivier Gourdon.

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**Education and Mentoring**

*Undergraduate participation:*

Evan Benbow: NSF Solid State Chemistry Summer Program; "Synthesis and structural characterization of new Ce-Ni-Al and La-Ni-Al compounds;" now a Graduate Student at Florida St. University.

Tim Barker: NSF-REU Program at ISU; "Electronic Structure Calculations of Complex Intermetallics," Junior at St. Olaf's College, MN.

Melissa Fierke: NSF-REU Program at ISU; "Electronic Structure Calculations on Doped ZnSb," Junior at Minnesota St. (Mankato, MN)

*Graduate Participation:*

Mi-Kyung Han, Cathie Condron, and Hyunjin Ko.

**International Activities**

Visiting Professor at Max-Planck-Institut for Solid State Research, Stuttgart, Germany

Agreement with Wiley-Interscience to write a monograph

*Chemistry and Physics of Intermetallic Compounds*